



Efficient preparation of 5-hydroxymethylfurfural from cellulose in a biphasic system over hafnium phosphates

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ABSTRACT

A series of hafnium phosphates $\text{HfO}(\text{PO}_4)_x$ ($x = 1.0, 1.5$ and 2.0) were prepared by coprecipitation of HfCl_4 with KH_2PO_4 , which were explored for efficient production of HMF from cellulose in $\text{NaCl-H}_2\text{O/THF}$ biphasic system. An excellent HMF yield of 69.8% was achieved over $\text{HfO}(\text{PO}_4)_{2.0}$ at 190°C for 240 min. Levulinic acid was barely produced during the reaction since the strength of $\text{HfO}(\text{PO}_4)_{2.0}$ is not enough to rehydrate HMF, and humins deposition was almost eliminated due to its poorer HMF adsorption (9.3 mg/g). The results showed that the role of the phosphate group in the catalyst could be in deactivation of unselective Lewis acid sites. Furthermore, high yields of HMF from other carbohydrates such as fructose (94.8%), glucose (90.5%), cellobiose (79.3%), sucrose (86.6%), starch (75.3%), inulin (80.4%), as well as wheat straw (18.6%) could be achieved using $\text{HfO}(\text{PO}_4)_{2.0}$ as a catalyst. During catalyst recyclable test, the catalytic performance of $\text{HfO}(\text{PO}_4)_{2.0}$ is well maintained after five catalytic cycles. Characterization analysis of fresh and recycled $\text{HfO}(\text{PO}_4)_{2.0}$ with SEM, XRD, and FT-IR indicated the catalyst has good stability and robustness.

1. Introduction

Due to the depleting fossil fuel reserves and increasing greenhouse gas emission, the exploration of feasible pathways for the conversion of abundant and renewable biomass into platform chemicals is highly desirable [1–4]. Among the carbohydrate based platform chemicals, 5-hydroxymethylfurfural (HMF) is identified as an important platform chemical due to it is widely used as a versatile building block for the production of fine chemicals, fuels, and monomers of polymers [5–9]. The widespread interest in HMF has promoted extensive studies on its synthesis [10–12]. Simple carbohydrates such as fructose and glucose can be conveniently dehydrated to HMF over various homogeneous and heterogeneous acid catalysts in monophasic or biphasic systems [13–15]. Although excellent yield of HMF could be achievable from monosaccharide, using cellulose, a more abundant and less expensive carbohydrates, to produce HMF has received considerable interest [16]. However, the conversion cellulose into HMF often gives poor HMF yield due to the robust structure of cellulose [17,18], and instability of HMF under harsh reaction condition [19].

To facilitate the process of cellulose-to-HMF conversion, ionic liquid

has been used as a novel solvent due to its remarkable ability to dissolve cellulose [11,20]. In 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl), 55.4% yield of HMF was achieved from cellulose when using CuCl_2 and CrCl_3 as the catalysts at $80\text{--}120^\circ\text{C}$ [21]. Around 60% yield of HMF was synthesized from cellulose in 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) over the catalysts of CrCl_3 and metal chloride (LaCl_3 , LiCl , or LiBr) [22]. However, this system still suffers from the high price of ionic liquid and the separation problems between the HMF and ionic liquid [23,24]. Recent studies have been focused on the HMF synthesis in a biphasic system, in which a water-immiscible (or saltwater-immiscible) organic solvent is used to extract the produced HMF from the aqueous phase [13,23], and suppress the side reactions of HMF rehydration/decomposition/polymerization [25]. A series of biphasic systems have been reported for the synthesis of HMF from fructose or glucose [26–28], however, the direct transformation of cellulose into HMF in a biphasic system remains a challenge due to the poor reactivity of cellulose [29], and the key to achieving this goal is the development of efficient and robust catalysts.

Transition metal oxides are water-tolerant and property-tunable solid acids, which were widely used in HMF production, particularly,

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TiO₂ and ZrO₂ have been reported to show high activities for the synthesis of HMF [30–38]. Atanda et al. investigated HMF production from cellulose over phosphated TiO₂, a modest HMF yield of 33% was obtained in NaCl-H₂O/THF biphasic system, the yield of HMF could be increased to 86% when the cellulose was pretreated by mechanocatalytic depolymerization [30]. In another of their work, 25.5% yield of HMF could be obtained from cellulose over TiO₂-ZrO₂ combined with Amb-15 in NaCl-H₂O/THF biphasic system [36]. Similar to zirconium and titanium, hafnium can also be used to prepare strong acid catalyst [39], however, to the best of our knowledge, there are few works concentrated on HMF production with hafnium base catalyst. Recently, Zhang et al. reported that using hafnium (IV) chloride as a catalyst for the production of HMF from glucose in [Bmim]Cl, and 76.7% yield of HMF was achieved at 100 °C in 60 min [40]. Hu et al. demonstrated that 98% yield of HMF could be obtained from fructose in dimethylsulfoxide (DMSO) over Hf-MOF catalyst at 100 °C in 60 min [41]. However, neither of the above hafnium base catalysts can effectively catalyze the conversion of cellulose to HMF.

Herein, a series of hafnium phosphates HfO(PO₄)_x were prepared by coprecipitation of HfCl₄ with KH₂PO₄, and explored for the efficient production of HMF from cellulose in a biphasic NaCl-H₂O/THF medium. Analysis techniques such as ICP-OES, XRD, TEM, N₂ adsorption-desorption, FTIR of adsorbed pyridine, and NH₃-TPD were employed to characterize the structure and properties of the synthesized catalysts. The activities of catalysts with different ratio of P/Hf were investigated to balance the hydrolysis, isomerization, and dehydration in the process of cellulose conversion to HMF. The reaction conditions including the solvent system, reaction temperature, time, and catalyst dosage were studied in detail to improve the yield of HMF. In addition, HMF production from other carbohydrate was also investigated. Finally, the recyclability of the catalyst was evaluated by leaching and reusing tests on the glucose dehydration.

2. Experimental

2.1. Materials

Microcrystalline cellulose (98%), glucose (98%), fructose (99%), and potassium dihydrogen phosphate (KH₂PO₄, 97%) were analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). HMF (> 99%, chromatographic grade) and hafnium chloride (HfCl₄, 98%) were obtained from Sigma (Shanghai, China). Other reagents and solvents were analytical grade and used without further purification unless otherwise noted.

2.2. Catalyst characterization

The elemental analysis was tested using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Agilent 720). X-ray diffraction (XRD) patterns of the catalysts were recorded in the range of 10° ≤ 2θ ≤ 90° on Rigaku SmartLab. N₂ adsorption-desorption was obtained on TriStar II 3020 (Micromeritics, America). The surface area was calculated by the Brunauer-Emmett-Teller (BET) method and the total pore volume was estimated by the Barrett-Joyner-Halenda (BJH) at P/P₀ = 0.99. TEM micrographs were recorded on an FEI Tecnai G2 F20 transmission electron microscope (FEI, America). The acidity properties of catalysts were identified by pyridine infrared spectroscopy analysis on Nicolet 380 (Thermo Fisher Scientific, America). The amount and strength of the acid sites on the catalysts were detected by NH₃-TPD was performed on a TP-5080 (Xianquan Industrial and Trading Co., Ltd., Tianjin, China).

2.3. Catalysts preparation

Hafnium hydroxide hydrate was prepared by using HfCl₄ as the hafnium source through neutral amine sol-gel method. Typically,

ammonium hydroxide solution was added by dropwise into the aqueous solution of HfCl₄ (10 mmol in 50 mL deionized water) under stirring until the pH of the mixture reached to 8–9. The mixture was further stirred for 2 h at room temperature and then aged at 120 °C for 6 h. The catalyst was recovered through filtration, and then dried at 80 °C overnight after removing the extra ion by thorough washing with water and alcohol.

Hafnium phosphates were prepared by coprecipitation of HfCl₄ with KH₂PO₄. Typically, KH₂PO₄ solution (designed amount in 50 mL deionized water) was added by dropwise into the aqueous solution of HfCl₄ (10 mmol in 50 mL deionized water) under stirring. The mixture was further stirred for 2 h at room temperature and then aged at 120 °C for 6 h. The catalyst was recovered through filtration, and then dried at 80 °C overnight after removing the extra ion by thorough washing with water and alcohol.

Samples were calcined under air atmosphere at 550 °C for 4 h (10 °C/min). The hafnium phosphates were designated as HfO(PO₄)_x, x represents the ratio of P to Hf.

2.4. Catalytic reactions and analysis method

For conversion of cellulose in H₂O/THF system, a mixture of cellulose (0.1 g, 0.62 mmol, based on glucose unit), catalyst (0.03 g, 30 wt %), NaCl (0.20 g) and solvent (5 mL, water/THF, 1:4, v/v) were loaded into flask. After sealed the flask, put the reaction vessel into the oil bath which preheated to the designed temperature to react for the desired time. After the reaction, the reaction mixture was cooled to room temperature through the air cooling, the reaction mixture presented three-phase: the upper layer is the THF layer containing HMF; the medium layer is the aqueous layer containing NaCl, oligosaccharide, glucose, and fructose, the bottom layer consists of unconverted cellulose and the catalyst (Fig. S1).

Products were analyzed by high-performance liquid chromatography (HPLC) (HPLC, Agilent 1260 series, Hewlett-Packard, USA) equipped with RID 1260 detectors using Bio-Rad Aminex HPX-87H* (300 nm × 7.8 mm, catalog #125-0140) column at 55 °C using 5 mM H₂SO₄ as the mobile phase at a flow rate of 0.6 mL/min. The cellulose conversion (wt%), and HMF yield (mol%) were calculated basis on the following formulas:

Cellulose conversion (wt%):

$$\text{Cellulose conversion} = \left(1 - \frac{\text{mass of remaining cellulose}}{\text{mass of starting cellulose}} \right) \times 100 \quad (1)$$

Remaining cellulose = Mount of solid content reaction – mount of catalyst loaded (2)

HMF yield (mol%):

$$\begin{aligned} \text{HMF yield} &= \frac{\text{moles of HMF in product}}{\text{moles of cellulose loaded in the reaction (base on glucose unit)}} \times 100 \end{aligned} \quad (3)$$

HMF selectivity (mol%):

$$\begin{aligned} \text{HMF selectivity} &= \frac{\text{moles of HMF in product}}{\text{moles of cellulose converted (base on glucose unit)}} \\ &\times 100 \end{aligned} \quad (4)$$

3. Results and discussion

3.1. Catalyst characterization

Results of the ICP-OES analyses of the catalysts were listed in Table 1. The P/Hf ratio of catalysts based on ICP-OES is in accordance

Table 1
Elemental analysis of catalysts.

Entrys	Molar ratio of P/Hf input	ICP-OES			Designation of catalyst
		P (%)	Hf (%)	P/Hf	
1	1.0	10.82	61.48	1.01	HfO(PO ₄) _{1.0}
2	1.5	14.02	52.83	1.53	HfO(PO ₄) _{1.5}
3	2.0	15.64	46.69	1.93	HfO(PO ₄) _{2.0}
4	2.5	15.57	46.56	1.93	HfO(PO ₄) _{2.0}

with the theoretical value when the ratio of P/Hf input in the range of 1–2. However, a maximum P/Hf ratio = 2 cannot be surpassed with further increasing the input of KH₂PO₄. The hafnium phosphate catalysts were designated as HfO(PO₄)_x, x represents the ratio of P to Hf according to the ICP-OES analysis.

The XRD patterns of HfO₂ and HfO(PO₄)_x showed that no evidence of the crystalline phases of the HfO₂ and HfO(PO₄)_x were formed (Fig. S2). This suggests that HfO₂ and HfO(PO₄)_x could be present in amorphous phase. The TEM images of the catalysts showed that the morphological features of catalysts are influenced by the incorporation of phosphates (Fig. S3). It is clearly observed that the particle size of HfO₂ (Fig. S3a) is much larger than that of HfO(PO₄)_x (Fig. S3 b–d), which can be used to explain the low *S*_{BET} of HfO₂ in comparison with HfO(PO₄)_x. The results of the N₂ adsorption-desorption isotherm of catalysts were presented in Table 2. The *S*_{BET} and pore volume of catalysts displays a sharp increase after phosphates incorporation. The isotherm of HfO₂ and HfO(PO₄)_x also shows a sharp increase in the volume of N₂ adsorption at a relative pressure of 0.55 and 0.80, which indicates that HfO₂ and HfO(PO₄)_x are characteristic for mesoporous structures (Fig. 1) [30]. Furthermore, with phosphates incorporation, the average pore diameter of the catalysts (determined by BJH measurement at *P*/*P*₀ = 0.99) increases significantly from 4.6837 nm (HfO₂) to 13.9848 nm (HfO(PO₄)_{2.0}), suggesting that the mass transfer limitation of catalyst could be reduced after phosphates incorporation.

Different types and strength of acidic sites on the catalysts were analyzed by Py-FTIR. Typically, the absorption band at around 1452 cm^{−1} and 1615 cm^{−1} indicates the pyridine on Lewis acid sites, while the band at 1537 cm^{−1} is assigned to pyridine on Brønsted acid sites [30,42]. As shown in Fig. 2a, HfO₂ is characterized by absence of absorption bands at 1537 cm^{−1}, which means HfO₂ is a pure Lewis acid catalyst (Fig. 2a). The detection of the band at 1537 cm^{−1} on HfO(PO₄)_x catalyst indicates that Brønsted acid sites were formed after incorporation of phosphate (Fig. 2b–d). The variable intensity of the spectrum band displays an alteration of Brønsted and Lewis acid sites concentration, the ratio of Brønsted (PyB) to Lewis (PyL) acid sites concentration was calculated on the basis of the extinction coefficients for bands at 1537 and 1452 cm^{−1} (Table 2) [43], and the results showed that the Brønsted acidity increases along with the increasing of molar ratio of P/Hf.

Table 2
Physical and acid properties of HfO₂ and HfO(PO₄)_x.

Entry	Sample	<i>S</i> _{BET} ^a (m ² /g)	Pore volume ^b (cm ³ /g)	Acidity ^c PyB/PyL (n/ n)	Acid density ^d (mmol/g)	
					Total	Strong
1	HfO ₂	130.78	0.1531	0	0.227	0.024
2	HfO(PO ₄) _{1.0}	175.14	0.3125	0.11	0.461	0.133
3	HfO(PO ₄) _{1.5}	209.13	0.4425	0.17	0.777	0.316
4	HfO(PO ₄) _{2.0}	240.03	0.6235	0.20	0.918	0.409

^a BET surface area.

^b Determined by Barrett-Joyner-Halenda (BJH) measurement at *P*/*P*₀ = 0.99.

^c Determined using the Lambert–Beer Law.

^d Determined by NH₃-TPD, total (100–550 °C), strong (300–550 °C).

The strength and amount of the acid sites on the surface of HfO₂ and HfO(PO₄)_x catalysts were further studied by NH₃-TPD. As shown in Fig. 3, the curves for NH₃-TPD between the range of 100–550 °C shows the ammonia desorption for all the samples, which corresponds to the medium and strong acid sites [44]. The curves for NH₃-TPD also show the influence of the phosphate incorporation on acidity of catalyst since the intensity of HfO(PO₄)_x was higher than HfO₂ in the ammonia desorption curve. The acid density of catalysts determined by TPD-NH₃ is presented in Table 2, the results show that the acid site density (both the medium and the strong acid sites) significantly enhanced after incorporation of phosphate.

3.2. Catalyst evaluation

3.2.1. Catalytic activity

Catalytic conversion of cellulose to HMF was first conducted by different catalysts including H₃PO₄, HfO₂, HfO(PO₄)_{1.0}, HfO(PO₄)_{1.5}, and HfO(PO₄)_{2.0}. The blank experiment showed that the conversion of cellulose was quite low under the reaction conditions (Table 3, entry 1) due to its robust structure [17,18]. H₃PO₄ presented 12.4% yield of HMF with 68.4% conversion of cellulose (Table 3, entry 2), the low selectivity (18.1%) of HMF suggesting that the conversion cellulose to HMF with only Brønsted acid is a low-efficient process [45,46], which is due to the fact that the activation energy of glucose (monomer of cellulose)-to-HMF is much higher than that of glucose-to-humins catalyzed by Brønsted acid [47,48]. As shown in the entries 3–6, the yield and selectivity of HMF both showed significant improvement over Hf-based catalyst, which can be explained by the conversion of glucose to HMF in presence of Lewis acid is a tandem process of isomerization and dehydration thus overcoming the thermodynamic constraints by lowering the activation energy of glucose-to-HMF through the fructose intermediate [48]. When using HfO₂ as the catalyst, 36.3% yield of HMF with 59.6% conversion of cellulose was obtained, however, the selectivity of HMF (60.9%) was not satisfactory due to the side-reactions of rehydration and polymerization of HMF to levulinic acid and humins [30,32,44]. This was further confirmed by the detection of levulinic acid during the reaction, and the change in color of HfO₂ from white to dark brown at the end of the reaction (Table 3 entry 3, Fig. 4 a_I and a_{II}). For HfO(PO₄)_x catalysts, the following order of reactivity was observed: HfO(PO₄)_{2.0} > HfO(PO₄)_{1.5} > HfO(PO₄)_{1.0}, which correlates with the *S*_{BET} and acid density of catalysts. It is worth mentioning that an impressive yield of 69.8% with 77.8% selectivity of HMF was achieved when using HfO(PO₄)_{2.0} as a catalyst (Table 3, entry 6). In addition, we measured the content of Na in HfO(PO₄)₂ by ICP-OES after the first cycle due to the high excess of NaCl in the reaction system, the result showed that the content of Na in HfO(PO₄)₂ after the first cycle is 0.33 wt%, which indicated that Na⁺ exchange with proton of the catalyst was occurred during the reaction. This catalyst was further reused in the reaction, and the result indicated that the catalytic performance of Na⁺ exchanged HfO(PO₄)₂ was almost the same as that of fresh HfO(PO₄)₂ (Table 2, entry 7). Given the facts above, we speculated that the role of Brønsted acidity of this catalyst is not so important due to the fact that pure HfO₂ also provided high selectivity 60.9% to HMF. Thus, the actual role of phosphate group could be in deactivation of unselective Hf-OH sites adsorbing HMF due to the excess of Lewis acidity on the catalyst leads to unselective glucose transformation into humins [44,49].

It's also worth mentioning that the formation of levulinic acid when using HfO(PO₄)_{2.0} as a catalyst under the present reaction condition was quite low (Table 3, entry 6). Previous works reported that the rehydration of HMF to levulinic acid normally requires strong acid conditions and long reaction time [50,51], which suggests that HfO(PO₄)_{2.0}, in spite of possessing a certain amount of strong acid sites, its strength is not enough to rehydrate HMF to levulinic acid.

Another advantage of using HfO(PO₄)_{2.0} as the catalyst is humins deposition was significantly reduced (Fig. 4 d_{II}). The humins deposition

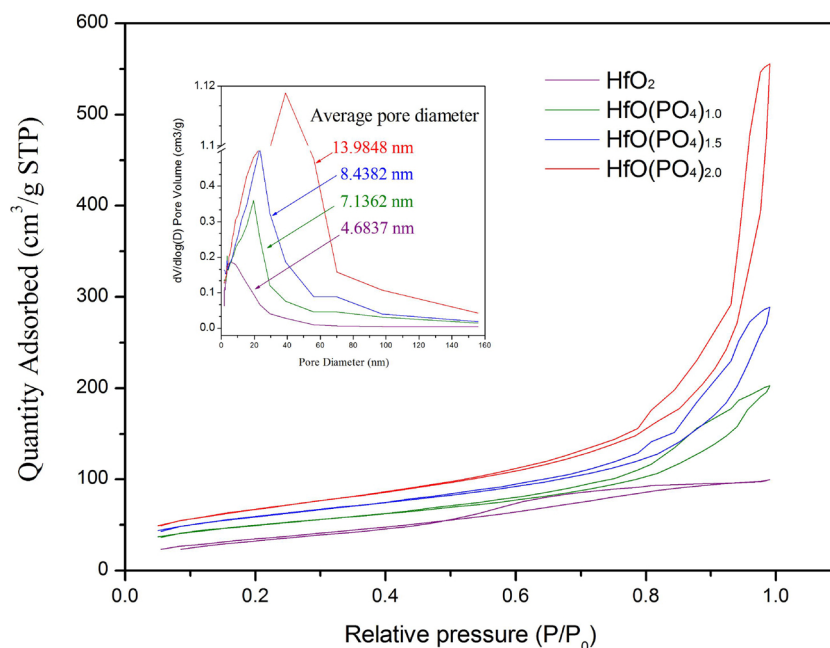
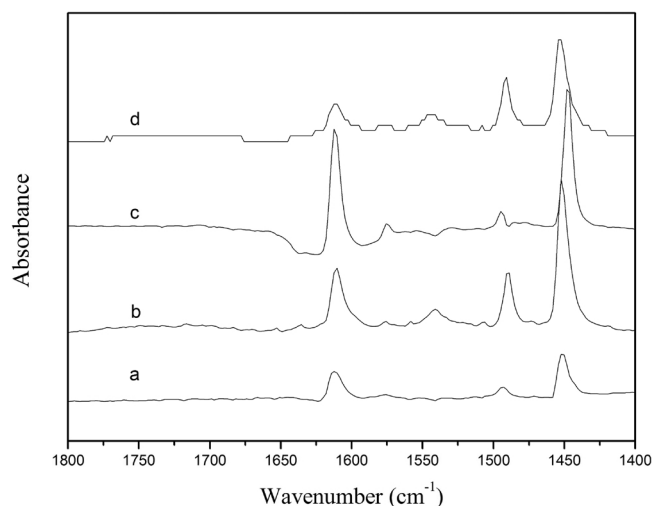


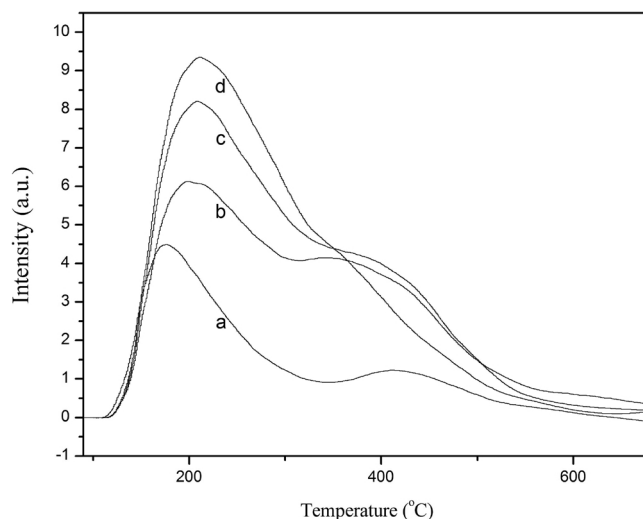
Fig. 1. Nitrogen adsorption-desorption isotherms.

Fig. 2. Py-FTIR spectra of (a) HfO_2 , (b) $\text{HfO}(\text{PO}_4)_{1.0}$, (c) $\text{HfO}(\text{PO}_4)_{1.5}$, and (d) $\text{HfO}(\text{PO}_4)_{2.0}$.

often becomes a big obstacle for the industrial application of solid acids [50,52]. We assumed that the humins deposition on catalyst surface was related to the HMF adsorption capacity of the catalysts. To check this point, the adsorption capacity of HMF on the catalyst was investigated, and the results were presented in Table 3, and the pictures of color change of the catalysts before and after reaction were also exhibited in Fig. 4. As shown in the Table 3, the $\text{HfO}(\text{PO}_4)_x$ shows much lower capacity of HMF absorption (9.3–45.3 mg/g) than that of HfO_2 (90.6 mg/g), which is consistent with the color change of the catalysts before and after reaction (Fig. 4). A plausible explanation for this phenomenon is the low absorption of HMF adsorption means low HMF concentration in micro-environment of the acids sites, which would reduce the side reaction of HMF polymerized to humins. Thus, the very poor HMF absorption ability of $\text{HfO}(\text{PO}_4)_{2.0}$ (9.3 mg/g) would be the dominant reason for the absence of humins deposition.

3.2.2. Reaction conditions

The effect of the different organic solvent on the production of HMF

Fig. 3. NH_3 -TPD spectra of (a) HfO_2 , (b) $\text{HfO}(\text{PO}_4)_{1.0}$, (c) $\text{HfO}(\text{PO}_4)_{1.5}$, and (d) $\text{HfO}(\text{PO}_4)_{2.0}$.

from cellulose using $\text{HfO}(\text{PO}_4)_{2.0}$ as the catalyst is shown in Fig. 5a. The HMF yield and cellulose conversion are in the order of MeTHF (71.9%, 90.9%) > dioxane (70.2%, 90.3%) > THF (69.8%, 89.7%) > MIBK (60.3%, 89.3%) > 1-butanol (59.6%, 88.3%) > 2-butanol (54.5%, 87.4%). Higher HMF yields and selectivity were obtained with cyclic ethers (MeTHF, dioxane, and THF) as the extractive phase, which could be attributed to the oxygen heterocyclic structure of cyclic ethers leading to an increased ability to extract the produced HMF. Among the cyclic ethers used in this work, THF was selected as the extraction solvent for the follow-up study due to its lower price than MeTHF, and lower energy-intensive for HMF separation than dioxane, although higher HMF yield were achieved in $\text{NaCl-H}_2\text{O/MeTHF}$ and $\text{NaCl-H}_2\text{O/dioxane}$ system.

The reaction temperature was further studied in the range of 145 °C to 205 °C with 15 °C interval. As shown in Fig. 5b, the HMF yield and cellulose conversion increased with the increasing of reaction temperature from 145 to 190 °C, indicates that higher temperature is beneficial for the conversion of cellulose over the $\text{HfO}(\text{PO}_4)_{2.0}$. Further

Table 3
Catalytic conversion of cellulose to HMF over HfO_2 and $\text{HfO}(\text{PO}_4)_x$.

Entry	catalyst	Cellulose conv. (%)	HMF yield ^a (%)	HMF select. (%)	HMF Adsorp. ^b (mg/g)
1	—	5.2	0.5	9.6	—
2	H_3PO_4	68.4	12.4	18.1	—
3	HfO_2	59.6	36.3 (9.8)	60.9	90.6
4	$\text{HfO}(\text{PO}_4)_{1.0}$	61.5	43.2 (6.3)	70.2	45.3
5	$\text{HfO}(\text{PO}_4)_{1.5}$	75.7	55.8 (3.6)	73.7	19.6
6	$\text{HfO}(\text{PO}_4)_{2.0}$	89.7	69.8 (< 0.5)	77.8	9.3
7	$\text{HfO}(\text{PO}_4)_{2.0}^c$	85.9	62.1	72.3	—

Reaction conditions: cellulose (0.10 g, 0.62 mmol, based on glucose unit), NaCl (0.20 g), catalyst (0.03 g), solvent (5.0 mL, $\text{H}_2\text{O}/\text{THF}$, 1:4 v/v), 190 °C, 240 min.

^a HMF yield in organic phase. Values in brackets are the yield of levulinic acid.

^b 60.0 mg catalyst added in HMF solution (60.0 mg in 2.0 mL H_2O) and stirred for 6 h. The amount of HMF adsorption was calculated by the HMF reduced in the solution.

^c The catalyst after the first cycle was reused.

increase the reaction temperature to 205 °C leads to a decrease in both HMF yield and selectivity, which may be ascribed to unfavorable side-reactions such as condensation of HMF or cross-polymerizations of HMF with reactive intermediates were occurred under this condition [50,53]. Thus, the optimal reaction temperature is set at 190 °C and used for subsequent experiments.

With regard to the loading of $\text{HfO}(\text{PO}_4)_{2.0}$, as shown in Fig. 5c, the cellulose conversion and HMF yield was increased by using an elevated catalyst dosage. However, further increased the catalyst loading exceeds 30 wt% shows no obvious improvement for the yield of HMF. Thus, the optimal dosage of $\text{HfO}(\text{PO}_4)_{2.0}$ dosage is regarded as 30 wt%, which was used for the subsequent experiments.

The kinetic study reveals that HMF yield and cellulose conversion increase along with the reaction time, where maxima values of 69.8% and 96.3% were achieved at 240 min and 300 min, respectively (Fig. 5d). Further extension of reaction time to 360 min has little effect on the cellulose conversion, meanwhile, the HMF yield was decreased to 60.9%, which probably due to the remarkable decomposition of HMF after a long reaction time [53]. Glucose and fructose, the dominating intermediates, were detected during the reaction and achieved the highest yield of 21.3% and 6.9% after 120 min and 150 min, respectively, suggesting that cellulose conversion to HMF over $\text{HfO}(\text{PO}_4)_{2.0}$

could be a tandem process of hydrolysis, isomerization, and dehydration [54].

3.2.3. Conversion of other carbohydrate

With the aim to verify the applicability of $\text{HfO}(\text{PO}_4)_{2.0}$, the present system was further examined for the conversion of other carbohydrates. As shown in Table 4, most substrate underwent smooth transformation to afford the corresponding HMF in moderate to excellent yields under the present system. The yield of HMF from starch (75.3%) proceeds higher than that from cellulose (69.8%), the disparity in the reactivity of starch and cellulose could be attributed to their different structure, for starch, the glucose units are linked through α -1,4 or α -1,6 linkages whereas the glucose units in cellulose are linked with an un-branched β -1,4 fashion, which is densely packed due to the strong hydrogen bonds and translates into inferior reactivity than starch [17,18]. High HMF yield of 80.4% could be achieved from inulin which is a polymer of fructose units linked by β -1,2 glucosidic bonds, which can be attributed to the high reactivity of fructose units than glucose units (entries 4 and 5) [50]. 79.3% and 86.6% yield of HMF were obtained from cellobiose and sucrose, respectively, the higher reactivity of disaccharide than polysaccharide maybe attributed to the difference in the solubility of these two carbohydrates [16]. The catalytic activity of $\text{HfO}(\text{PO}_4)_{2.0}$ was further tested for the conversion of the raw wheat straw, 18.6% yield of HMF and 7.3% yield of furfural were achieved under this nonoptimized condition. The poor reactivity of wheat straw can be attributed to the presence lignin, which can act as the physical barrier to prevent the contact of the catalyst with cellulose and hemicellulose.

3.3. Recyclability of the $\text{HfO}(\text{PO}_4)_{2.0}$

Acid sites leaching and deactivation, two major issues of catalyst recyclability in the HMF production [55,56], were investigated using glucose as a substrate since the heterogeneous nature of cellulose. Acid sites leaching test was conducted by $\text{HfO}(\text{PO}_4)_{2.0}$ filtration after running the glucose dehydration for about 60 min at 190 °C, and then continued the reaction to 240 min with the absence of $\text{HfO}(\text{PO}_4)_{2.0}$ catalyst. As shown in Fig. 6a, no further reaction is observed, indicating that no acid site of $\text{HfO}(\text{PO}_4)_{2.0}$ is leached. Stability of $\text{HfO}(\text{PO}_4)_{2.0}$ was further investigated by batch reaction of glucose dehydration in a $\text{NaCl}-\text{H}_2\text{O}/\text{THF}$ medium at 190 °C for a shorter reaction time of 60 min to evaluate the catalytic efficiency. After each reaction, the $\text{HfO}(\text{PO}_4)_{2.0}$ catalyst was recovered by filtration, washed with water and dried under vacuum at

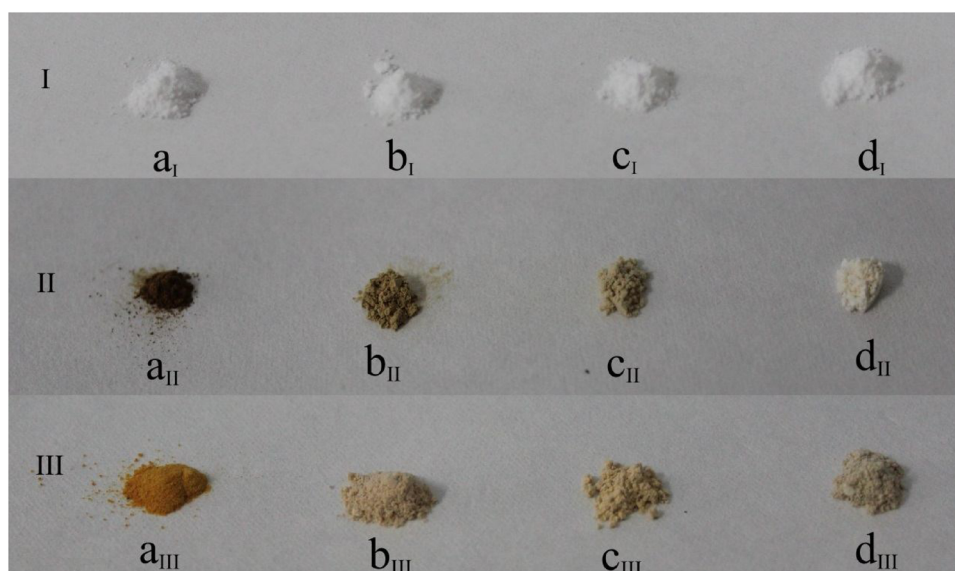


Fig. 4. Color changed of catalysts. I: fresh catalysts; II: after reaction; III: after HMF absorption. (a) HfO_2 , (b) $\text{HfO}(\text{PO}_4)_{1.0}$, (c) $\text{HfO}(\text{PO}_4)_{1.5}$, and (d) $\text{HfO}(\text{PO}_4)_{2.0}$.

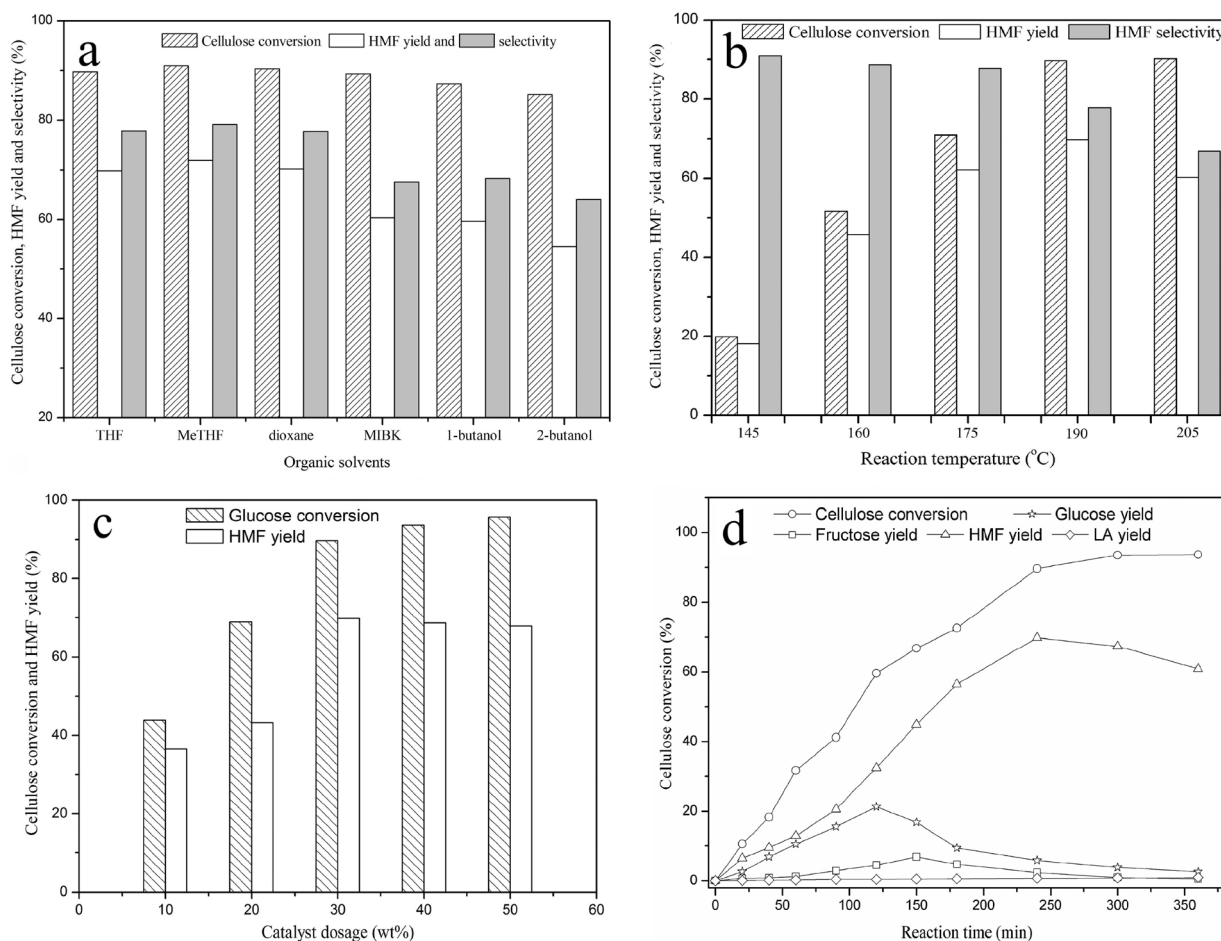


Fig. 5. Effect of reaction temperature (a) and time (b) on the cellulose conversion to HMF. Reaction conditions: cellulose (0.10 g), NaCl (0.20 g), $\text{HfO}(\text{PO}_4)_2 \cdot 0$ (0.03 g), solvent (5.0 mL, water/THF, 1:4 v/v). a: 240 min; b: 190 °C.

Table 4
Catalytic conversion of a variant of sugars to HMF over $\text{HfO}(\text{PO}_4)_2 \cdot 0$.

Entry	sugar	Temperature (°C)	Time (min)	Conv. (%)	HMF yield (%)
1	cellulose	190	240	89.7	69.8
2	starch	190	240	91.2	75.3
3	inulin	190	240	96.3	80.4
4	fructose	160	120	99.5	94.8
5	glucose	175	150	99.7	90.5
6	cellobiose	175	180	98.1	79.3
7	sucrose	175	180	98.7	86.6
8	wheat straw	190	240	41.6	18.6(7.3) ^a

Reaction conditions: sugar (0.10 g), NaCl (0.20 g), $\text{HfO}(\text{PO}_4)_2 \cdot 0$ (0.03 g), solvent (5.0 mL, water/THF, 1:4 v/v).

^a Values in brackets is the yield of furfural.

80 °C for overnight, and then used for next run. Excitingly, no apparent loss of catalytic activity was observed even after five times recycling (Fig. 6b).

The fresh and five times reused $\text{HfO}(\text{PO}_4)_2 \cdot 0$ catalyst were further characterized by SEM, XRD, and FT-IR. As shown in the TEM (Fig. 7a, b) images, the structure of the recovered catalyst did not collapse and the particles showed no obvious aggregation compared to the fresh catalyst. Meanwhile, from the patterns of XRD (Fig. 7c) and FT-IR (Fig. 7d), it can be seen that the recovered catalyst showed the same characteristic peaks to the fresh one, which indicates that the structure of the recovered catalyst is not changed. In addition, the ratio of Hf/P in the $\text{HfO}(\text{PO}_4)_2 \cdot 0$ after five cycles was 1.90 according to ICP-OES

analysis, which is close to that in the fresh catalyst (1.93), suggesting that no apparent leaching of phosphate was occurred during the reaction. The carbon content in the catalyst after reuse was also calculated by calcination, the result showed that the carbon content in the catalyst after five cycles was 0.04%, which indicates the carbon accumulation was almost non-existent.

4. Conclusions

In summary, a series of $\text{HfO}(\text{PO}_4)_x$ have been designed and synthesized by coprecipitation of HfCl_4 with KH_2PO_4 . Among them, $\text{HfO}(\text{PO}_4)_2 \cdot 0$ was found to be an efficient heterogeneous acid catalyst for the conversion of cellulose to HMF. High efficiency and selectivity, strong ability to resist carbon accumulation, good applicability and recyclability was observed for the present catalyst. Future work about further applications of this catalyst is currently under investigation in our group.

Declarations of interest

None

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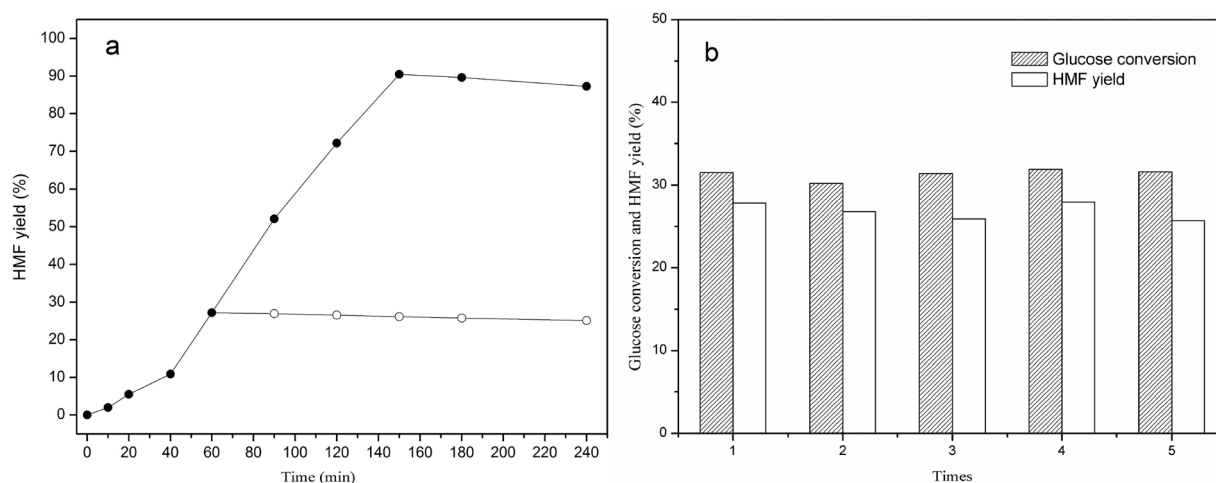


Fig. 6. Time-yield plots of glucose-to-HMF conversion existence $\text{HfO}(\text{PO}_4)_2$ (solid circle) or removing $\text{HfO}(\text{PO}_4)_2$ after 60 min (hollow circle) (a) and recyclability of the $\text{HfO}(\text{PO}_4)_2$ for glucose dehydration (b). Reaction conditions: glucose (0.10 g), NaCl (0.20 g), $\text{HfO}(\text{PO}_4)_2$ (0.03 g), solvent (5.0 mL, water/THF, 1:4 v/v), reaction temperature 190 °C; b: 60 min.

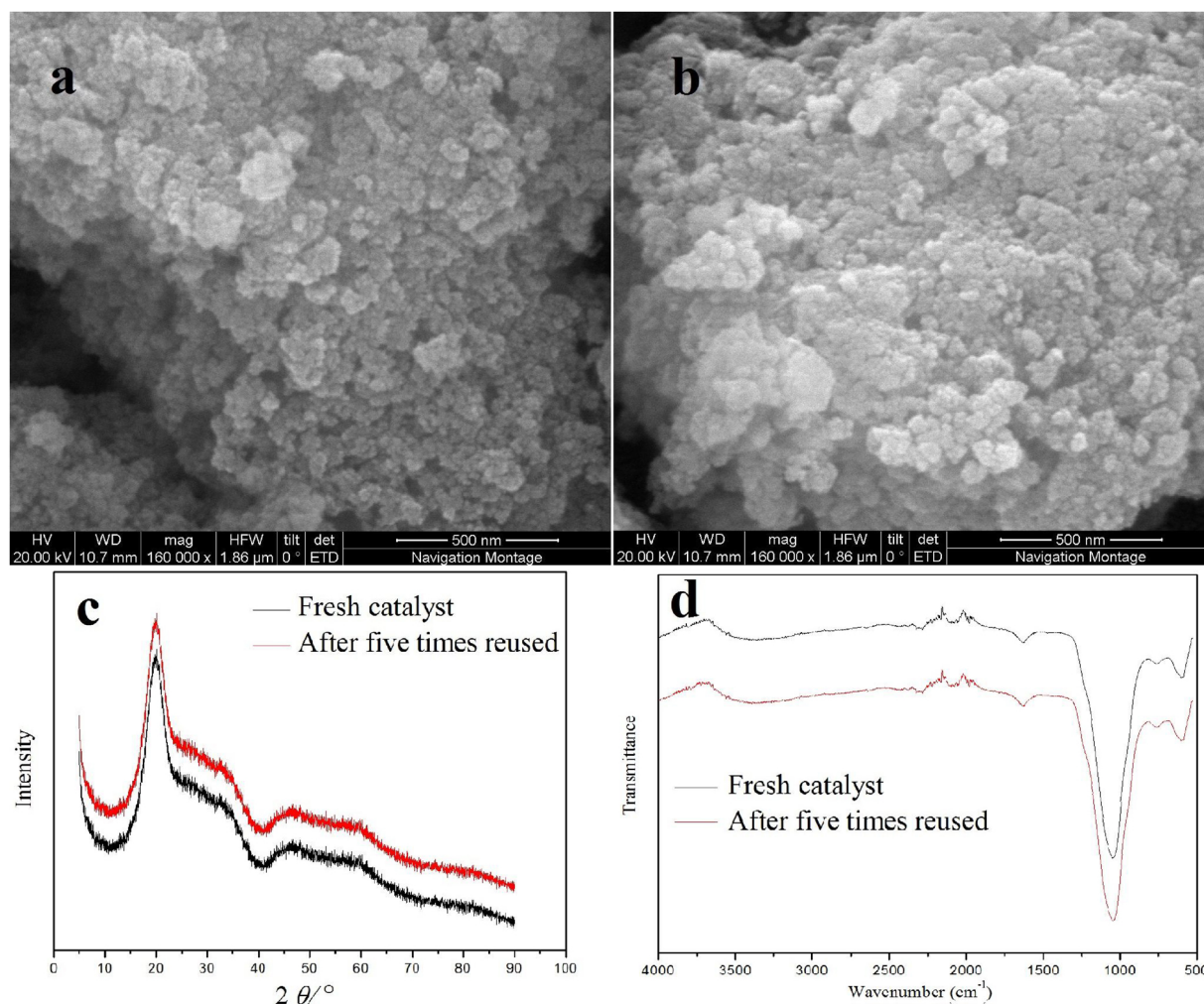


Fig. 7. SEM (a: fresh catalyst; b: after five times reused), XRD (c), and FT-IR (d) patterns of $\text{HfO}(\text{PO}_4)_2$.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2018.11.019>.

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